A Novel Luminescent μ_4-Selenido-Bridged Copper(I) Tetramer

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A novel soluble tetranuclear copper(I) cluster containing an unsubstituted μ_4-selenido moiety, $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})]^{2+}$ (**1**), has been synthesized and characterized by X-ray crystallography. Its photophysical and electrochemical properties have been studied. It is envisaged that the emissions of **1** are associated with a ligand-to-metal charge-transfer LMCT $[(Se^{2-}) \rightarrow Cu_4]$ triplet excited state, and probably with mixing of a metal-centered $(3d^94s^1)$ Cu(I) state. The phosphorescent state of **1** undergoes facile electron-transfer quenching with a series of pyridinium acceptors. An excited-state reduction potential, $E°[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})^{3+/2+*}]$, of −1.55(10) V *vs* SSCE has been estimated. Crystal data: monoclinic, space group *C*2/*c* (No. 15), $a = 27.913(9)$ Å, $b = 16.512(9)$ Å, $c = 24.10(1)$ Å, $\beta = 109.29(2)°$, $V = 10483(5)$ Å^3, $Z = 4$.

Introduction

The chemistry of transition metal−chalcogenide complexes represents an important aspect in structural chemistry owing to the highly flexible bonding modes of the ligands.[1] Despite structural information on a number of transition metal−selenium clusters such as those of palladium, iridium, nickel, and cobalt[1c] being known, photochemical studies on related complexes remain very limited. Recently, Fenske *et al*. reported the syntheses and structural characterizations of a series of high-nuclearity copper−selenium clusters with monodentate phosphine ligands.[2] These large Cu−Se clusters were found to be sparingly soluble in common organic solvents after crystallization, and this inevitably limits their potentials for chemical studies. Current interests are being focused, both experimentally and theoretically, on the identities of the reaction intermediates in the syntheses of these clusters.[2d,3] In view of this, together with our recent successful isolation and characterization of the first luminescent sulfido-copper(I) complex,[4] we believe that an exploration to related selenido clusters might establish a new class of soluble luminescent materials. Herein, we report on the synthesis, characterization, and X-ray crystal structure of the first luminescent copper(I)−selenium cluster $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})]^{2+}$ (**1**). Its photophysical, photo−redox and electrochemical properties have also been studied.

Experimental Section

$[Cu_2(\mu\text{-dppm})_2(MeCN)_2](PF_6)_2$ was prepared by a reported method.[5] Lithium selenide was obtained by dissolving stoichiometric amounts of Li and Se in liquid ammonia. All solvents were purified and distilled by standard procedures before use. All reactions were carried out using standard Schlenk techniques. The pyridinium salts were prepared by refluxing the corresponding substituted pyridine with the appropriate alkylating reagent such as CH_3I in acetone−ethanol (1:1 v/v) for 4 h, followed by metathesis in water using NH_4PF_6 and recrystallization from acetonitrile−diethyl ether.

Preparation of $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})](PF_6)_2$ (1). To a stirred solution of $[Cu_2(\mu\text{-dppm})_2(MeCN)_2](PF_6)_2$ (86.4 mg, 0.068 mmol) in acetone (10 mL) was added freshly prepared Li_2Se solid (3.17 mg, 0.034 mmol). The solution immediately turned to orange-yellow with the appearance of some black precipitate. Stirring was continued for 15 min, and the solution was filtered, partially evaporated and carefully layered with diethyl ether. $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})](PF_6)_2$ was isolated as an air-stable orange-yellow crystal (67.8 mg, 0.031 mmol, 92% yield). Positive ESI-MS: ion clusters: *m*/*z* 933.5, $[Cu_4(dppm)_4(Se)]^{2+}$; 2012 $\{[Cu_4(dppm)_4(Se)](PF_6)\}^+$. ^1H NMR (270 MHz, acetone-d_6, 298 K, relative to TMS): δ 3.6 (m, 8H, methylene H's), 7.1−7.7 (m, 80H, phenyl H's).

Physical Measurements and Instrumentation. UV−visible spectra were obtained on a Hewlett−Packard 8452A diode array spectrophotometer, steady state emission spectra on a Spex Fluorolog 111 spectrofluorometer. Low temperature (77 K) spectra were recorded by using an optical Dewar sample holder. ^1H NMR spectra were recorded on a JEOL JNM-GSX270 Fourier-transform NMR spectrometer. Positive ion ESI mass spectra were recorded on a Finnigan MAT95 mass spectrometer.

Emission-lifetime measurements were performed using a conventional laser system. The excitation source was the 355-nm output (third harmonic) of a Quanta-Ray Q-switched GCR-150−10 pulsed Nd-YAG laser (10 Hz). Luminescence decay signals were recorded on a Tektronix Model TDS 620A digital oscilloscope and analyzed using a program for exponential fits. All solutions for photophysical studies were prepared under vacuum in a 10-cm^3 round-bottomed flask equipped with a side arm 1-cm fluorescence cuvette and sealed from the atmosphere by a Kontes quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze−pump−thaw cycles. Luminescence quenching experiments were monitored by time-resolved (lifetime) emission measurements, and data were treated by a Stern-Volmer fit as described by $\tau_o/\tau = 1 + k_q\tau_o$ [Q], where τ_o and τ are the respective excited-state lifetimes in the absence and presence of quencher Q, respectively. k_q is the bimolecular quenching rate constant and [Q] is the concentration of the quencher.

Cyclic voltammetric measurements were performed by using a Princeton Applied Research (PAR) universal programmer (Model 175) and potentiostat (Model 173). The ferrocenium−ferrocene couple was used as the internal standard in the electrochemical measurements in acetonitrile (0.1 mol dm^{-3} $^nBu_4NPF_6$). The working electrode was a glassy carbon (Atomergic Chemetals V25) electrode with a platinum foil acting as the counter electrode.

Crystal Structure Determination. Single crystals of **1** were

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

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Table 1. Crystal and Structure Determination Data for **1**

formula	$[Cu_4SeP_8C_{100}H_{88}]^{2+}\ 2PF_6^{-}\cdot(CH_3)_2CO\cdot 2H_2O$
M_r	2254.77
T, K	298
a, Å	27.913(9)
b, Å	16.512(9)
c, Å	24.10(1)
β, deg	109.29(2)
V, Å^3	10483(5)
cryst color and shape	yellow prism
cryst syst	monoclinic
space group	$C2/c$ (No. 15)
Z	4
$F(000)$	4592
D_c, g cm^{-3}	1.429
cryst dimens, mm	0.15 × 0.15 × 0.25
λ, Å (graphite monochromated, MoKα)	0.71073
μ, cm^{-1}	13.69
collcn range	$2\theta_{max} = 45°$ (h: 0−30; k: 0−18; l: −26 to 26)
scan mode; scan speed, deg min^{-1}	$\omega-2\theta$; 16
scan width, deg	$0.68 + 0.35 \tan\theta$
no. of data collcd	7320
no of unique data	7145
no. of data used in refinement, m	2393
no. of params refined, p	315
R^a	0.080
$R_w{}^a$	0.083
goodness-of-fit, S	2.85
max shift, $(\Delta/\sigma)_{max}$	0.05 (for the cation)
residual extrema in final diff map, e Å^{-3}	+0.92, −0.80

[a] $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.013F_o^2)^2]$ with $I > 3\sigma(I)$.

obtained by layering of diethyl ether onto a concentrated acetone solution of the complex. Diffraction data for **1** were measured at 25 °C on a Rigaku AFC7R diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). Three standard reflections measured after every 300 reflections showed a decay of 1.38%. The intensity data were corrected for decay and for Lorentz and polarization effects, and empirical absorption corrections based on the ψ-scan of four strong reflections. Crystal and structure determination data for **1** are summarized in Table 1. The space group was determined from systematic absences and confirmed by the successful refinement of the structure solved by heavy-atom Patterson methods and expanded using Fourier techniques[6a] and refinement by full-matrix least squares using the MSC-Crystal Structure Package TeXsan[6b] on a Silicon Graphics Indy computer. The two halves of complex cation are related by symmetry with the Se(1) atom at a special position. A unit cell thus contains four complex divalent cations, eight PF_6^- anions, four acetone molecules and eight water molecules. As the crystal was not strongly diffracting and the number of observed reflections rather small, only the Se, Cu, and P atoms and the two bridging C atoms were refined anisotropically. The remaining 50 C atoms and the F and O atoms were refined isotropically. The 47 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined and the H atoms of the water molecule were not found. The final agreement factors for **1** are given in Table 1. The final atomic coordinates and thermal parameters for the non-hydrogen atoms are collected in Table 2.

Table 2. Atomic Coordinates and Thermal Parameters for Non-Hydrogen Atoms of **1**

atom	x	y	z	B_{eq},^{a} Å^2
Se(1)	0.5000	0.1783(2)	0.2500	3.58(9)
Cu(1)	0.44837(10)	0.2410(2)	0.2992(1)	3.75(8)
Cu(2)	0.5585(1)	0.2309(2)	0.3388(1)	3.97(8)
P(1)	0.4159(2)	0.3661(4)	0.2816(3)	3.7(2)
P(2)	0.4401(2)	0.1523(4)	0.3677(3)	3.9(2)
P(3)	0.5558(2)	0.1496(4)	0.4127(3)	4.4(2)
P(4)	0.6229(2)	0.3165(4)	0.3466(3)	3.7(2)
P(5)	0.8551(5)	0.1901(9)	0.1925(8)	12.8(5)
F(1)	0.865(1)	0.163(3)	0.256(2)	28(1)
F(2)	0.849(1)	0.231(2)	0.135(2)	33(1)
F(3)	0.909(1)	0.185(2)	0.208(1)	22(1)
F(4)	0.854(1)	0.103(2)	0.175(2)	25(1)
F(5)	0.799(1)	0.183(2)	0.178(1)	19.3(10)
F(6)	0.852(2)	0.269(3)	0.224(2)	31(1)
O(1)	0.5000	0.053(2)	0.7500	13(1)
O(2)	0.229(1)	0.241(2)	0.521(1)	21(1)
C(1)	0.6044(8)	0.401(1)	0.2960(9)	4.1(7)
C(2)	0.4977(8)	0.089(2)	0.3927(9)	4.2(7)
C(3)	0.4620(8)	0.442(1)	0.3194(10)	4.3(6)
C(4)	0.4937(9)	0.419(2)	0.375(1)	5.6(6)
C(5)	0.530(1)	0.477(2)	0.409(1)	8.8(9)
C(6)	0.532(1)	0.551(2)	0.386(1)	8.3(9)
C(7)	0.501(1)	0.573(2)	0.335(1)	8.3(8)
C(8)	0.4645(9)	0.521(2)	0.299(1)	5.5(6)
C(9)	0.3604(9)	0.385(2)	0.3034(10)	4.7(6)
C(10)	0.3501(10)	0.464(2)	0.318(1)	6.8(7)
C(11)	0.309(1)	0.478(2)	0.338(1)	9.5(9)
C(12)	0.2810(10)	0.413(2)	0.342(1)	7.1(8)
C(13)	0.2894(10)	0.336(2)	0.331(1)	6.7(7)
C(14)	0.3318(9)	0.324(1)	0.3113(10)	5.0(6)
C(15)	0.4314(8)	0.184(1)	0.4351(9)	4.1(5)
C(16)	0.4232(9)	0.268(2)	0.445(1)	6.6(7)
C(17)	0.414(1)	0.295(2)	0.493(1)	8.7(9)
C(18)	0.4166(9)	0.239(2)	0.537(1)	6.8(7)
C(19)	0.4263(10)	0.161(2)	0.532(1)	7.7(8)
C(20)	0.4333(9)	0.130(2)	0.480(1)	6.3(7)
C(21)	0.3882(9)	0.076(1)	0.3398(10)	4.6(6)
C(22)	0.346(1)	0.084(2)	0.357(1)	7.7(8)
C(23)	0.306(1)	0.026(2)	0.332(1)	9.3(9)
C(24)	0.312(1)	−0.031(2)	0.299(1)	8.0(8)
C(25)	0.351(1)	−0.039(2)	0.280(1)	7.9(8)
C(26)	0.3939(10)	0.016(2)	0.301(1)	6.8(7)
C(27)	0.6048(10)	0.071(2)	0.421(1)	5.9(6)
C(28)	0.5991(10)	0.023(2)	0.373(1)	7.0(7)
C(29)	0.637(1)	−0.037(2)	0.377(1)	9.1(9)
C(30)	0.674(1)	−0.041(2)	0.427(2)	9.8(10)
C(31)	0.684(1)	0.001(2)	0.476(2)	11(1)
C(32)	0.646(1)	0.066(2)	0.474(1)	8.9(9)
C(33)	0.5648(8)	0.186(2)	0.4868(10)	4.7(6)
C(34)	0.5660(10)	0.131(2)	0.534(1)	7.3(8)
C(35)	0.574(1)	0.167(2)	0.590(1)	7.9(8)
C(36)	0.5793(10)	0.245(2)	0.597(1)	8.1(8)
C(37)	0.578(1)	0.300(2)	0.554(1)	8.1(8)
C(38)	0.5694(9)	0.268(2)	0.498(1)	7.1(7)
C(39)	0.6755(8)	0.268(1)	0.3294(9)	3.8(5)
C(40)	0.6712(9)	0.190(2)	0.314(1)	6.2(7)
C(41)	0.711(1)	0.151(2)	0.300(1)	7.1(7)
C(42)	0.756(1)	0.197(2)	0.308(1)	7.3(8)
C(43)	0.7619(9)	0.270(2)	0.328(1)	6.1(7)
C(44)	0.7212(9)	0.307(1)	0.3396(10)	5.4(6)
C(45)	0.6548(8)	0.360(2)	0.419(1)	4.5(6)
C(46)	0.679(1)	0.307(2)	0.463(1)	7.5(8)
C(47)	0.706(1)	0.331(2)	0.521(1)	9.7(9)
C(48)	0.702(1)	0.413(2)	0.527(1)	9.9(10)
C(49)	0.683(1)	0.472(2)	0.488(2)	10(1)
C(50)	0.6574(10)	0.442(2)	0.429(1)	6.7(7)
C(51)	0.5000	0.125(3)	0.7500	7(1)
C(52)	0.498(1)	0.165(2)	0.801(1)	11(1)

[a] B_{eq} is defined as $(8/3)\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

Results and Discussion

Unlike the preparations of high-nuclearity copper−selenium clusters by CuCl and $(Me_3Si)_2Se$,[2] complex **1** was synthesized by the reaction between $[Cu_2(\mu\text{-dppm})_2(MeCN)_2](PF_6)_2$ and Li_2Se in acetone. The orange-yellow complex was characterized by positive ESI-MS and ^{1}H NMR spectroscopy. The structure

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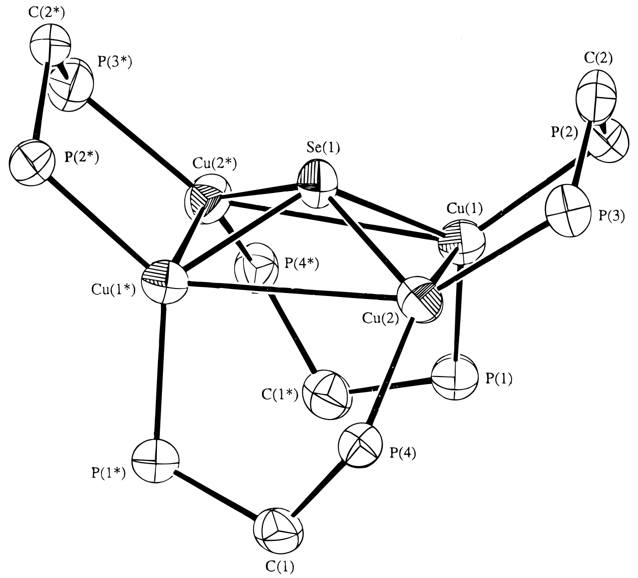

Figure 1. Perspective view of $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})]^{2+}$ with atomic numbering scheme. The phenyl rings are omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level.

Table 3. Selected Geometric Data for **1**

Selected Bond Lengths (Å)			
Cu(1)−Cu(2)	2.908(4)	Cu(1)−Cu(2*)[a]	3.271(4)
Cu(1)−Se(1)	2.384(3)	Cu(1)−P(1)	2.239(7)
Cu(1)−P(2)	2.276(7)	Cu(2)−Se(1)	2.387(3)
Cu(2)−P(3)	2.252(7)	Cu(2)−P(4)	2.245(7)
Selected Bond Angles (deg)			
Cu(1)−Se(1)−Cu(1*)	128.5(2)	Cu(1)−Se(1)−Cu(2)	75.1(1)
Cu(1)−Se(1)−Cu(2*)	86.6(1)	Cu(2)−Se(1)−Cu(2*)	137.3(2)
Se(1)−Cu(1)−P(1)	125.5(2)	Se(1)−Cu(1)−P(2)	107.7(2)
P(1)−Cu(1)−P(2)	126.8(3)	Se(1)−Cu(2)−P(3)	107.5(2)
Se(1)−Cu(2)−P(4)	126.6(2)	P(3)−Cu(2)−P(4)	123.0(3)

[a] Starred atoms with coordinates at $(1 - x, y, {}^1\!/_2 - z)$.

of $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})](PF_6)_2$ has also been established by X-ray crystallography.

Figure 1 depicts the perspective drawing of the complex cation $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})]^{2+}$ with atomic numbering. Selected bond distances and angles are summarized in Table 3. The four copper(I) ions form a distorted rectangular base, with an unsubstituted selenido ligand situated at *ca.* 0.95 Å above the idealized Cu_4 plane. The Cu−Cu distances in **1** range from 2.908(4) to 3.271(4) Å, comparable to those observed in $[Cu_3(dppm)_3(\mu_3\text{-Cl})_2]^+$ [3.175(4)−3.281(3) Å],[7a] $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-OH})]^{2+}$ [3.120(2)−3.322(2) Å],[7b] but significantly longer than those in $[Cu_{30}Se_{15}(P^iPr_3)_{12}]$ [2.52(1)−2.60(1) Å], $[Cu_{29}Se_{15}(P^iPr_3)_{12}]$ [2.714(5)−2.844(5) Å], and $[Cu_{36}Se_{18}(P^tBu_3)_{12}]$ [2.502(5)−2.889(5) Å].[2a] The Cu−Se bond distances [2.384(3)−2.387(3) Å] in **1** agree well with those observed in other selenido- and selenolato-copper(I) systems such as $[Cu_{70}Se_{35}(PEt_3)_{22}]$ [$Cu-\mu_4\text{-Se}$ = 2.336(5)−2.401(5) Å],[2b] $[Cu_{146}Se_{73}(PPh_3)_{30}]$ ($Cu-\mu_4\text{-Se}$ = 2.361−2.482 Å),[2c] $\{Cu[Se(2,4,6\text{-}Pr^i{}_3C_6H_2)]\}_6$ [Cu−Se = 2.370(2)−2.412(2) Å],[7c] and $[Cu_4(Se_4)_{2.4}(Se_5)_{0.6}]^{2-}$ [2.37(3) Å].[7d] The Cu−Se−Cu bond angles in **1** between two adjacent Cu(I) ions are in the range of 75.1(1)−86.6(1)°, slightly smaller than the corresponding Cu−S−Cu angles in **2** [78.45(5)−87.19(7)°].[4] The four dppm ligands are arranged in a manner such that an opposite-pair is located above the Cu_4 plane while the other pair below it. It is interesting to note that the interatomic distance between the methylene carbons C(1) and C(1*) [*ca.* 5.51 Å] is substantially shorter than that between C(2) and C(2*) [*ca.* 6.92 Å]. This is also in line with the shorter bond distance of Cu(1)−Cu(2) [2.908(4) Å] than that of Cu(1*)−Cu(2) [3.271(4) Å]. This observation may be attributed to the steric requirements of the selenido ligand as well as the bulky phenyl rings. The Cu−P bond distances are typical of those reported in other Cu(I)−dppm complexes.[7a,b] It is worth mentioning that the Cu(1)−P(2) and Cu(2)−P(3) bond distances [2.276(7) and 2.252(7) Å] are longer than those of Cu(1)−P(1) and Cu(2)−P(4) [2.239(7) and 2.245(7) Å]. This is reasonable considering the fact that the Cu(1)−P(2) and Cu(2)−P(3) bonds and the bulky selenido ligand all lie on the same side of the Cu_4 plane while the Cu(1)−P(1) and Cu(2)−P(4) lie on the other side.

Table 4. Photophysical Data for **1**

abs[a] λ, nm (ϵ, $dm^3\,mol^{-1}\,cm^{-1}$)	medium (T, K)	emission λ, nm	τ_o, μs
262 sh (42670)	solid (298)	595	3.9 ± 0.2
	solid (77)	619	
	glass (77)[b]	478, 608	
	$(CH_3)_2CO$ (298)	626	7.1 ± 0.2
	CH_3CN (298)	622	6.9 ± 0.2

[a] In MeCN at 298 K. [b] Acetone:methanol:ethanol = 1:1:4.

The electronic absorption spectrum of **1** in CH_3CN reveals a high energy absorption shoulder at *ca.* 262 nm and a lower energy absorption in the 350−450 nm region. The high-energy absorption band is assigned as intraligand IL (dppm) transitions.

Excitation of **1** in solid state and fluid solutions with $\lambda >$ 350 nm results in intense long-lived orange luminescence. The photophysical data of **1** are summarized in Table 4. On the basis of the good σ-donating capability of the chalcogenide ion, the transitions are assigned to originate predominantly from a ligand-to-metal charge-transfer LMCT[$(Se^{2-}) \rightarrow Cu_4$] triplet excited state, probably with mixing of a metal-centered ($3d^9$-$4s^1$) Cu(I) state. Similar assignments have also been suggested in $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-S})]^{2+}$,[4] as well as other luminescent polynuclear d^{10} halo[8a,b] and thiolato[8c−e] clusters. The long-lived solid-state luminescence of **1** (595 nm) occurs at a lower energy than that of its sulfido counterpart (579 nm), and this supports the assignment that the excited states of these chalcogenido tetranuclear copper(I) clusters would bear a high parentage of LMCT[$(E^{2-}) \rightarrow Cu_4$] triplet character, considering the fact that the filled ligand-based orbitals are at lower energy for sulfide than selenide. However, in fluid solutions, their emission energies are quite similar (for example, in acetone, $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-E})]^{2+}$ emits at 622 nm [E = S] and 626 nm [E = Se], respectively).

The phosphorescence of **1** in acetone was found to be quenched by a number of electron acceptors. In order to understand the electron-transfer reactivity of the excited state of **1**, a study of electron-transfer quenching by a series of pyridinium acceptors of variable reduction potentials was carried out. The bimolecular quenching rate constants are listed in Table 5. An excited-state reduction potential, $E°[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})^{3+/2+*}]$ of −1.55(10) V *vs* sodium chloride calomel electrode (SSCE) [$\lambda = 1.12(10)$ eV, $RT(\ln K)\kappa\nu = 0.61(10)$ V *vs* SSCE] has been estimated by three-parameter, nonlinear least-squares fits to eq 1, where $k_{q'}$ is the rate constant corrected for diffusional effects, $K = k_d/k_{-d}$ which is approximately 1−2 dm^3

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Table 5. Bimolecular Rate Constants for the Oxidative Quenching of $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})]^{2+*}$ by Pyridinium Acceptors in Degassed Acetone (0.1 mol dm^{-3} $^nBu_4NPF_6$)

quencher[a]	$E(A^{+/0})$, V (vs SSCE)	k_q, dm^3 mol^{-1} s^{-1}	$k_{q'}$, dm^3 mol^{-1} s^{-1} [b]
4-cyano-*N*-methylpyridinium	-0.67	5.35×10^9	1.15×10^{10}
4-(methoxycarbonyl)-*N*-methylpyridinium	-0.78	3.39×10^9	5.13×10^9
4-(aminoformyl)-*N*-ethylpyridinium	-0.93	1.76×10^9	2.14×10^9
3-(aminoformyl)-*N*-methylpyridinium	-1.14	2.12×10^8	2.17×10^8
N-ethylpyridinium	-1.36	1.02×10^7	1.02×10^7
4-methyl-*N*-methylpyridinium	-1.49	0.98×10^6	0.98×10^6

[a] All the compounds are hexafluorophosphate salts. [b] $(1/k_q') = (1/k_q) - (1/k_d)$, where k_d is the diffusion-limited rate constant, taken to be 1.0×10^{10} dm^3 mol^{-1} s^{-1}.

$$(RT/F) \ln k_{q'} = (RT/F) \ln K \kappa \nu - (\lambda/4)(1 + \Delta G/\lambda)^2 \quad (1)$$

mol^{-1}, k_d is the diffusion-limited rate constant which is taken to be 1.0×10^{10} dm^3 $mol^{-1}s^{-1}$, κ is the transmission coefficient, ν is the nuclear frequency, and λ is the reorganization energy for electron transfer, and ΔG, the standard free energy change of the reaction, which is given by eq 2 for oxidative quenching,

$$\Delta G = E°[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})^{3+/2+*}] - E°(A^{+/0}) + \omega_r - \omega_p \quad (2)$$

where ω_r and ω_p are work terms for bringing reactants or products to the mean separation for reaction. This contribution is neglected in the analysis of the electron-transfer rate data. A plot of ln $k_{q'}$ *vs* $E(A^{+/0})$ for the oxidative quenching of $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})]^{2+*}$ is shown in Figure 2. The close agreement between the theoretical curve with the experimental data is in accordance with the fact that the photoreactions are outer-sphere electron transfer in nature. It is also envisaged that **1** is a strong reductant in the excited state in view of its high excited-state reduction potential.

Cyclic voltammetric studies of **1** in MeCN (0.1 mol dm^{-3} $^nBu_4NPF_6$) reveal irreversible oxidation waves at +0.24, +1.05 and +1.24 V *vs* Fc^+/Fc. The irreversible nature of the redox waves suggests that the oxidized form of the cluster is not stable within the time scale of the cyclic voltammetric experiments.

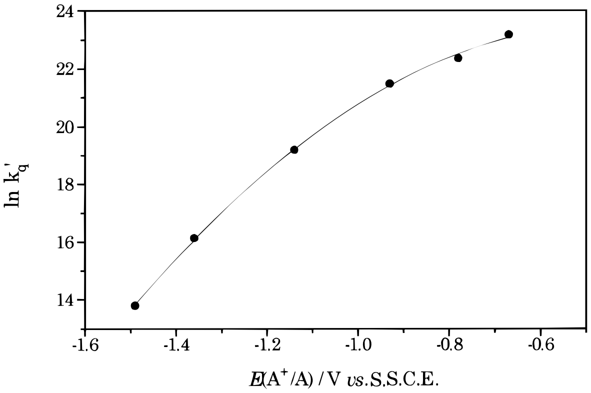

Figure 2. Plot of ln $k_{q'}$ *vs* $E(A^{+/0})$ for the electron-transfer quenching of $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})]^{2+*}$ by pyridinium acceptors in degassed acetone: (●) experimental; (—) calculated, where $k_{q'}$ is the rate constant corrected for diffusional effects.

The present work demonstrates the first example of a soluble copper(I)−selenido cluster which has been shown to possess rich photophysical and photochemical properties. Studies on related luminescent clusters are in progress.

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Supporting Information Available: Text giving details of crystal structure solution and tables giving fractional coordinates and thermal parameters for all atoms, general displacement parameter expressions U, and complete lists of bond distances and bond angles (13 pages). Ordering information is given on any current masthead page.

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